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Chemical Structures of Group 4 Metal Crosslinkers for Polygalactomannans

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Abstract

In SPE 37280 and SPE 39531,* Harry et al., and Moorhouse, et al., respectively, demonstrated that seemingly minor variations in aqueous based crosslinker chemistry can produce significant differences in the rheological responses of polygalactomannan-based fracturing fluids crosslinked with these agents. While the work contained some references to boron crosslinking and the principle conclusion can be applied to both boron and zirconium fracturing fluid systems, the emphasis was on zirconium crosslinked systems. Not surprisingly, some of the observed differences in performance could be attributed to variations in the crosslinker chemistry. Crosslinker differences that were isolated and evaluated included differences in the ligand chemistry, the ligand-to-metal-ratio, the nature of the zirconium starting material, etc. Moorhouse, et al., suggested several mechanisms by which these phenomena might be explained. The authors stopped short, however, of making any attempt to correlate the chemical structure of the crosslinker with its rheological performance.

With this paper the authors advance their studies to present a more comprehensive examination of the proposed structures of titanium and zirconium alkoxides and aqueous-based chelates, including a general discussion of the methods employed to manufacture these crosslinkers and factors present in Group 4 metal crosslinkers that may affect their

crosslinking response with polygalactomannans. There is also some discussion on other methods that have been employed to control the gelation rate. Finally, there is some discussion on the effects of polymer attributes to fracturing fluid performance, particularly as it relates to crosslinker efficacy.

The findings presented in the paper are supported by laboratory analyses that includes the examination of crosslinking agents by nuclear magnetic resonance (NMR) imaging, X-ray crystallography, and the rheological performance evaluation of systematically altered crosslinking agents. The authors suggest chemical structures of titanium and zirconium compounds used to crosslink polygalactomannans as supported by the findings of the analytical evaluations already mentioned.

Introduction

This paper is *not* a presentation of data that will serve to demonstrate that a particular Group 4 metal is superior to the others for use as a crosslinking agent to gel polygalactomannans for use as fracturing fluids. The data presented herein will also *not* demonstrate that Group 4 alkoxides are superior to Group 4 chelates, or vice versa. Nor will the data presented herein serve to support a contention that some particular Group 4 starting material, chelate, or ligand-to-metal ratio is superior to some other. The data presented herein does support the conclusion that there are performance differences among the various Group 4 crosslinkers, and that these differences can be attributed to the crosslinker composition as well as to the environment in which it is applied.

From our earlier work with zirconates¹, the authors have been able to conclude, not surprisingly, that (all other things in the fracturing fluid composition being equal) variations in crosslinker loadings will produce tremendous differences in fluid performance. Also not surprising was the demonstration that variations in polymer type (e.g., guar, HPG, CMHPG, CMG) will produce significant differences in fluid performance. Polymers cannot be used interchangeably in the same fluid system without optimization of the components that comprise the fluid system. Perhaps somewhat more surprising was the conclusion that polymers from different sources can produce significant differences in fluid

* SPE 37280, "Rheological Responses to Variations in Aqueous-Based Zirconium Crosslinker Chemistry," 1997 SPE International Symposium on Oilfield Chemistry. SPE 39531, "Inter-relationships between Polymer-Crosslinker Chemistry and Performance in Fracturing Fluids," 1998 SPE India Oil and Gas Conference and Exhibition.

performance; i.e., the "same" chemical composition does not guarantee the same performance. While it might be expected that guar as provided to different industries (such as food, textile, or explosives) may be processed to intentionally produce materials different from those used in fracturing, it was not expected that high viscosity guar (or guar derivatives reported to possess the same kinds and degrees of substitution) would provide for such significantly different results as were observed. However, they did, and the differences between the "same" polymers generally became greater as test conditions became more severe, e.g., as the pH was lowered or the test temperature raised. It could be concluded that low test-temperatures and/or high alkalinity served to "neutralize" the polymeric attributes that accentuated the differences under the more severe test conditions.

Likewise, it was demonstrated² that variations in the zirconium raw material source (for example, comparisons between chloride, sulfate, and carbonate zirconium sources) in the manufacture of zirconium crosslinkers identical in all other respects can produce significant differences in fracturing fluid performance. It was also demonstrated that variations in the cation source, such as where one cation is an alkali-earth and the other is an amine, can produce significant differences in fracturing fluid performance.

Particular fracturing fluid chemistries have an optimum pH at which the maximum performance for that particular fluid chemistry can be attained. Likewise, particular fracturing fluid chemistries have a pH range over which they are suitable and outside of which they may fail miserably. Variations in the chemical composition of the ligand, as well as the ratio of ligand-to-metal were also shown to produce substantial performance differences.³

If we could conclude but one thing for our previous work, it would be that due to the innumerable variations possible in fracturing fluid chemistry, even where the comparative chemistries are likely to be regarded as functionally equivalent, *it is best to select a fracturing fluid based upon performance criteria.* To assume that a desired fluid performance can be achieved by simply requesting a particular chemistry is a prescription for failure. A rose may be a rose by any other name, but not all zirconium crosslinked CMHPG's are created the same.

Group 4 Metals

The Group 4 metals of particular interest to the pumping services industry are titanium, zirconium, and hafnium. Of the more than 2.3 million patents issued since 1971, nearly 50,000 include at least some mention of a Group 4 metal, but only about 1000 deal with a Group 4 metal as a crosslinker. Of these 1000 patents, approximately 63% deal with titanium, 33% with zirconium, and only 4% with hafnium. Probably because of the widespread availability of suitable titanium products, titanium was the first Group 4 metal to find widespread use as a crosslinker in fracturing applications. The Group 4 metal most often used today as a crosslinker for polygalactomannans is zirconium. Hafnium, although nominally represented in the patent literature, has yet to

establish itself as a commercially viable alternative to titanium or zirconium in fracturing applications. Thus far, work with hafnium crosslinkers has yet to produce any definable benefit to commercializing hafnium as an alternative to titanium or zirconium.

Since zirconium and hafnium are always found together in nature, special methods have been developed to isolate these metals where it is essential that the other not be present. Since the isolation process can represent a substantial cost to the user, and since the presence of hafnium has not been shown to cause a deleterious effect to zirconium crosslinker performance in fracturing applications, the zirconium crosslinkers used by the pumping services industry inherently contain a small amount of hafnium.⁴ Since the hafnium present in the zirconium stock used to manufacture crosslinkers is subjected to the same processes as the zirconium stock, it is felt that a small portion of the "zirconium" crosslinker is actually present as a hafnium crosslinker. Consequently, it is likely that some small portion of the crosslinking observed in the gelation of galactomannans could be attributed to hafnium. For example, the authors believe that a certain amount of sodium-hafnium-lactate is present in a sodium-zirconium-lactate crosslinker by virtue of the small percentage of hafnium present in the zirconium stock. However, since, to the best of the authors knowledge, there has been no demonstration thus far that hafnium is in any way superior to titanium or zirconium as a crosslinker in hydraulic fracturing applications, our discussion will focus primarily on titanium and zirconium.

Group 4 Metal Crosslinkers

The typical titanium and zirconium crosslinkers used in fracturing are water-soluble complexes containing chelating ligands derived from functionalized amines (such as alkanolamines), functionalized carboxylic acids (such as the alpha-hydroxycarboxylic acids), and beta-diketones (such as acetylacetone). These chelated crosslinkers can be prepared from the inorganic metal tetrachlorides, metal sulfates or metal carbonates (where these forms exist), or from ortho-titanate or ortho-zirconate esters. Although some forms are not known or are not well described, water solubility of Group 4 metal salts can be placed in the series:



The Group 4 metal crosslinking compounds are often referred to as *organo-metallic* crosslinkers by virtue of their being "organically" chelated. However, since these crosslinkers do not possess a carbon-metal bond, they are more properly described as metal esters or chelates.

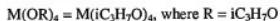
Crosslinker Manufacture. Where Group 4 metal tetrachlorides (MCl_4) are used as starting materials, a fully substituted alkoxide (Fig. 1) can be prepared (eq. 1) by

* In all natural occurrences, hafnium is usually present within the range 1.5 to 3% by weight of zirconium.

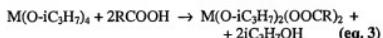
reacting the Group 4 metal tetrachloride with an alcohol (ROH) in the presence of a hydrogen chloride acceptor, such as ammonia (NH_3).



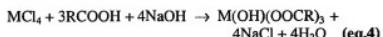
The commercially available alcohol-based crosslinkers are prepared (eq. 2) by reacting an ortho-metallic ester, such as tetra-isopropyl titanate or tetra-n-propyl zirconate, with a chelating ligand, such as an alkanolamine or acetylacetone. A by-product alcohol, such as isopropyl or n-propyl alcohol, is left in the final product. It was by this manufacturing method that some of the earliest zirconium crosslinkers were introduced to the oil field pumping services' industry. More detailed description of the application of this art to the manufacture of crosslinkers for fracturing applications may be found in the patent literature.⁴



Metal acylates can be prepared (eq. 3) by reacting, for instance, the tetra-isopropoxide metal complex with a functionalized carboxylic acid. In this fashion, titanium tetraisopropoxide reacted with lactic acid forms titanium lactate and isopropyl alcohol. Under certain process conditions, water can be added to the complex, the alcohol removed by distillation and the pH of the alcohol-free aqueous solution adjusted with ammonium hydroxide to form a usable crosslinker.



Commercially available aqueous-based crosslinkers may also be prepared (eq. 4) by reacting the metal tetrachloride, such as titanium or zirconium tetrachloride, with a functionalized carboxylic acid.



These aqueous-based crosslinkers are typically prepared using alpha-hydroxycarboxylic acids, such as lactic acid, glycolic acid, or citric acid. By-product hydrochloric acid is neutralized with ammonium hydroxide, an alkali metal hydroxide, or an organic base. Often the organic base is an alkanolamine, such as triethanolamine, which may provide for additional chelation of the crosslinking metal. Other methods provide for the use of zirconium metal sulfates and carbonates as starting materials in the manufacture of crosslinkers.⁵

Crosslinker Evolution. It has long been known that orthotitanic acid is not stable as a monomer, but rather, rapidly polymerizes and subsequently precipitates as titanium dioxide.

In 1946, Henry L. Van Mater,⁶ in an effort to produce chemically neutral zirconium compounds for use in the personal care industry, observed that precipitated zirconium salts, such as zirconium lactate, could be made water-soluble by the addition of an alkali, such as ammonium hydroxide or an amine. Although he did not elaborate, Van Mater also disclosed that zirconium complexes of polyhydroxyl compounds could also be formed.

In the mid-1950's, Paul Lagally made a notable contribution toward the stabilization of titanium crosslinkers with the introduction of a novel preparation.⁷ Lagally found that stable monomers or low molecular weight polymers of titanium could be manufactured so that upon contact with water, polymerization and condensation of the metal would be suppressed. Lagally's titanates were stabilized by producing, among other forms, alkanolamine-chelated titanates.⁸ These compounds could be further stabilized in water by the addition of polyhydric alcohols, such as sorbitol or mannitol.

Lagally also found that his stable titanates could be hydrolyzed to control the release rate of the metal. Many of these hydrolyzing agents were acids. Lagally, in his examination of these acids, discovered, however, that certain acids were not useful as hydrolyzing agents because they had the opposite effect of forming stable titanium compounds. In particular, Lagally listed lactic and tartaric acids as unsuitable and concluded from the experience that all of the alpha-hydroxycarboxylic acids performed in this fashion. At approximately the same time, Charles A. Russel was forming very similar conclusions with both titanium and zirconium.⁸

Joseph D. Chrisp was probably the first to use aqueous-stable Group 4 metals as crosslinkers for polygalactomannans.⁹ Although Chrisp's application was for the explosives industry, his discovery, in the early 1960's, that aqueous-stable Group 4 metals could be used to cause gelation of polygalactomannan solutions would have considerable impact on the oilwell fracturing industry. Chrisp advanced Lagally's work by examining the intentional use of alpha-hydroxycarboxylic acids as ligands to enhance the stability of the metal compound in water. Chrisp also offered chemical structures of titanium-lactic acid chelates, titanium-acetylacetone chelates, and titanium-triethanolamine chelates to reflect the earliest thinking as to what he perceived the molecule to look like. Chrisp's original titanium-bis-triethanolamine chelate and a more modern representation of Chrisp's view re-drawn to reflect the cage-like structure are reproduced in Figure-2. Note that the alkoxy [OR] groups are shown attached directly to the metal. Such a structure

* Arnold J. Gelarie (U.S.P. 1,905,848; issued Apr. 25, 1933) probably should be credited for being the first to develop a Group IV metal amine chelate. His zirconium citrate hexamethylene-tetramine complex was water-soluble and reported to be an effective treatment for a number of human diseases. The authors do not recommend their products be used in Gelarie's applications, but rather request that you seek a physician's advice for treatment of any disease from which you might be suffering.

necessarily implies that the nature of the alkoxyl group would influence crosslinker performance properties.

Subsequent structural characterization by proton and C13 NMR¹⁰ suggests that the actual structure contains the six equivalent oxygen atoms found on the two triethanolamine molecules coordinated to titanium in an octahedral configuration. Since the molecule is electrically neutral, two hydrogen atoms are most likely bonded to one of the oxygen pairs (Fig. 3). This structure can account for the comparatively slow hydrolysis of the bis-triethanolamine titanate complex as compared to simple titanium tetraalkoxides (Fig. 1) such as tetra-isopropyl titanate, which rapidly forms a white precipitate of hydrated titanium oxide upon addition to water.

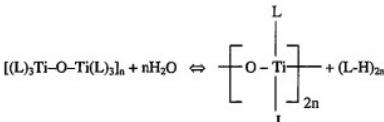
However, differences in the ratio of triethanolamine to metal may produce considerable performance differences. A comparison of the work performed independently by Williams¹¹ and, later, Kucera¹² would also seem to support this. The amine to metal ratio, however, appears to be significant, even though the number of amines chelating the metal cannot exceed four and is not likely to exceed two. The presence of an excessive quantity of amines may play a more important role in the stabilization of the polymer.¹³

With respect to the influence of the alcohol on the performance of the Group IV metal complex, if the Chrisep structure is correct (Fig. 2), then bis-triethanolamine titanate complexes derived from tetra-n-butyl titanate and tetra-2-ethylhexyl titanate should perform differently in that they should comprise different complexes. If the bis-triethanolamine titanate complex prepared from the tetra-isopropyl titanate is actually an isopropyl alcohol solution of the titanium complex (Fig. 3), then bis-triethanolamine complexes derived from tetra-n-butyttitanate and tetra-2-ethylhexyltitanate should contain the same complex in their respective by-product alcohol solutions and therefore show similar crosslinking behavior. The latter has indeed been shown to be the case (Table-1, Examples 12 & 13).

Further evidence to support the structure suggested by NMR spectra¹⁴ are performance evaluations of n-propyl zirconate crosslinkers formulated with n-propanol compared with n-propyl zirconate crosslinkers formulated with isopropanol. Comparative high temperature rheological performance evaluations produce no performance differences beyond those normally associated with test error.¹⁵

Addition of water to the bis-triethanolamine titanate complex just prior to use has been shown to significantly slow its rate of crosslinking (Table-1). On standing, this aqueous solution gradually loses crosslinking effectiveness, until after 12 hours it is no longer capable of generating significant

viscosity. The progression shown below (eq. 5) illustrates what is believed to happen when a hypothetical titanium complex, $Ti(L)_4$, comes into contact with water.



The first step involves displacement of one mole of ligand L with water to form one mole of free ligand (L-H) and a titanate complex containing one hydroxyl group, HO-Ti(L). This complex can react with another mole of titanate complex to form $(L)_3Ti - O - Ti(L)_3$, a mu-oxo dimer; and with additional water to form oligomeric titanium oxide chains and/or lattices (See Fig. 4). These oxide chains eventually lose all their water-solubilizing ligands and precipitate from solution. This is what Lagally observed and measured by determining the percent of light transmittance versus time.

Metal Complexes in Water. Tiner,¹⁶ in his effort to produce a Group 4 metal crosslinked galactomannan hydraulic fracturing fluid was probably the first to observe that the influence of water on the alcohol-based Group 4 metal complexes was different from that of alcohol. The addition of alcohol to titanate complexes to form field-strength crosslinkers did not produce a substantial change in structure, and may even have contributed to the stabilizing effect of the complex in water since the alcohol competes with water for metal bonding sites. It has been suggested that perhaps the alcohol forms a protective layer of solvation around the crosslinker that moderates the water reaction.¹⁷ Water, on the other hand, results in localized hydrolysis to produce a less reactive system through the formation of oligomers.

It has been proposed that these oligomers may play a role in crosslinking, where the solvent based crosslinker is added to an aqueous, and particularly alkaline, solution. It is suggested that oligomerization may continue, until such time as a colloid (See Fig. 5) is formed and that the colloid, in turn, may interact with the polymer to cause gelation.¹⁸ The reduction in crosslinker efficiency is believed to be a direct result of colloid formation, wherein significant portions of the crosslinking metal may be rendered incapable of performing the crosslinking function.

The addition of water is believed to initiate a reaction that continually changes the crosslinker composition so that it behaves differently with time until such time as the crosslinker is hydrolyzed to a point where it no longer retains activity.

Group 4 Metal Chelates

Generally, four types of chelating agents have been employed to minimize the rate of hydrolysis of the metal complexes. These methods directly relate to the crosslinking reaction rate observed in the gelation of polygalactomannans used in fracturing fluids.

The first method is to form metal complexes incorporating functionalized amines, such as hydroxylalkylamines (like triethanolamine). Alkylamines (such as diethylamine), on the other hand, are not chelating agents. However, they can coordinate with Group 4 metals in some cases and provide limited additional stability in water. They are also alkaline, and therefore may contribute to the water solubility of Group 4 metal carboxylates when used in neutralization.

The second method is to form metal complexes incorporating functionalized carboxylic acids, such as the alpha-hydroxycarboxylic acids (e.g., lactic acid or citric acid).

The third method is to form polyhydroxyl complexes of the Group 4 metals.

The fourth method is to form complexes incorporating beta-diketones, such as acetylacetone.¹⁹

These methods have also been combined to form Group 4 mixed-ligand complexes, such as might be found when both an alkanolamine and an alpha-hydroxycarboxylic acid are used together, as in the case of triethanolamine zirconium lactate.

Group 4 Metal Alkanolamine Complexes. The addition of water to the mono-triethanolamine titanate complex forms a mu-oxo dimer (See Fig. 6), the structure of which has been confirmed by x-ray crystallography.²⁰ A similar titanium-oxygen bridge most likely occurs on the addition of water to the bis-triethanolamine complex. Further oligomerization similar to that shown in Equation-5 accounts for the gradual loss of crosslinking strength of the system. The tetra-hydroxylated ethylenediamine complexes of titanium (Fig. 7) have been observed to crosslink much more slowly than the bis-triethanolamine titanate complex, and to be more stable in aqueous solution.²¹ The structure of the tetra-hydroxylated ethylenediamine complex, confirmed by x-ray crystallography,²² suggests that the metal is more protected and therefore less susceptible to hydrolysis than in the bis-triethanolamine titanate complex.

A similar relationship holds true for alkanolamine derived tetra-n-propyl zirconate complexes (Figure-9). The bis-triethanolamine zirconate complex reacts more rapidly than the tetra-hydroxylated zirconate complex (Table-1, Examples 10 & 9, respectively).

In general, alkanolamine zirconate complexes will crosslink at a slower rate than alkanolamine titanate complexes and the gels produced will show higher thermal stability. The cause of this difference is being investigated.

Group 4 Metal Carboxylic Acid Complexes. The second method of chelation employed to minimize the rate of hydrolysis is to form metal complexes incorporating functionalized carboxylic acids. These functionalized

carboxylic acids may be alpha-hydroxycarboxylic acids, such as lactic acid, glycolic acid, citric acid, etc., or alpha-aminocarboxylic acids, such as glycine or bis-hydroxyethylglycine. These Group 4 metal carboxylic acid chelates may be regarded as generally being of two types, alcohol-based chelates or aqueous-based chelates.

The alcohol-based chelates are formed by reaction of an alpha-hydroxycarboxylic acid with an ortho-metallic ester. For example, a bis-ammonium lactate complex of titanium (ammonium titanium lactate) is formed by reaction of lactic acid with tetra-isopropyl titanate to form a complex in isopropyl alcohol. In the commercially available product, water is added to this complex and the isopropyl alcohol is removed by distillation. The pH of the resultant aqueous solution is adjusted with ammonium hydroxide.

The aqueous-based zirconium carboxylates are generally formed by one of three methods. One method²³ involves the formation of an aqueous-insoluble intermediate from zirconium sulfate, that is, in turn, solubilized in water. This reaction involves the addition of a base, which may be an alkali-metal hydroxide or an amine, so that the final form can either be an alkali-metal zirconium carboxylate or an amine zirconium carboxylate. Although there is no reason to believe that the process would not be suitable for the manufacture of other Group 4 metal chelates where appropriate metal salts are commercially available, the process is costly and generates considerable quantities of effluent.

A second method²⁴ to form aqueous-based zirconium chelates is the reaction of alpha-hydroxycarboxylic acid salts with a zirconium solution to produce a mildly acidic or basic solution of the corresponding zirconium alpha-hydroxycarboxylic chelate. Work is in progress to evaluate the merits of this process with respect to other Group 4 metals.

A third method to form aqueous-based zirconium chelates is to prepare them by reacting an alpha-hydroxycarboxylic acid directly with a zirconium oxychloride solution, neutralizing the by-product hydrochloric acid to form an alkali metal zirconate. Sodium zirconium lactate and sodium zirconium glycolate have been prepared in this fashion. Interestingly, proton and C13 NMR spectral analysis²⁵ of these crosslinkers suggest that only two of the three moles of the alpha-hydroxycarboxylic acid ligand present in solution are actually bound to zirconium. See Figure 9.

The structure of one solid component isolated from an acidified solution of sodium zirconium glycolate has been shown by x-ray crystallography²⁶ to be an hexameric bis-glycolic complex $\{[CH_2(OH)C(O)O]_2Zr(OH)_2\}_6$ (Fig. 10).

This suggests that on addition of a sodium zirconium glycolate complex to an acidic polymer base solution that an oligomerization process may begin prior to any crosslinking. The degree of oligomerization will undoubtedly influence the crosslinking rate and the strength of the resultant gel.

Stabilization of Aqueous Group 4 Metal Carboxylic Acid Chelates. It has been observed that zirconium lactate crosslinkers manufactured from different enantiomeric mixtures of lactic acid respond differently for some period of

time after manufacture, all other things being equal. It is known that levorotatory lactic acid is more soluble in water than the racemic mixture. The racemic mixture has, however, been found to generate aqueous zirconium chelates that react more consistently, and sooner, than zirconium chelates manufactured with levorotatory lactic acid. Upon aging, the crosslinkers gradually perform more closely alike, as if they had been manufactured with the same lactic acid.

Conway²⁷ and Almond²⁸ observed similar stabilization versus time effects where various polyols were used to stabilize aqueous based titanates and zirconates. A possible explanation for the enhanced stability upon aging, particularly where the crosslinker solution is alkaline, may be the result of a Lobry de Bruyn-type transformation where the carboxylic acid ligands may be susceptible to isomerization.²⁹ As the enantiomeric ligands transform to some constant ratio of one isomer to another for the chemical and physical conditions found in the crosslinker solution, the crosslinker performance under certain identical conditions becomes more consistent.

Lagally, in his early work, noted that "the epimeric sugar stabilizers glucose, mannose, and fructose undergo the Lobry de Brun transformation when they are allowed to stand with the alkaline amine titanate solution, before neutralization is performed." Perhaps this provides an explanation for the observations made by Conway and Almond in their work with polyols as delay agents for Group 4 metal crosslinkers.

The time required to reach comparable performance in a zirconium crosslinker manufactured using different enantiomeric mixtures of lactic acid is dependent upon the pH of the crosslinker solution and the ambient temperature. This serves to suggest that since the "racemic lactate" crosslinker achieves "asymptotic" performance before "levorotatory lactate" crosslinker, that the ultimate ratio of lactate isomers favors the condition found in the racemic mixture. As there is a lag-time between manufacture and stabilization of the lactic acid chelate, performance testing as a quality-control measure must be delayed until sufficient time for the stabilization of the crosslinker has passed.³⁰

Polyhydroxyl Complexes of Group 4 Metals. Although the very earliest work by Lagally and Russell incorporated the use of polyhydric alcohols to enhance the stabilization in water of titanates and zirconates, it was not until about 1980 that this early art was incorporated into the manufacture of crosslinkers for polygalactomannans. Conway,³¹ with titanates, and shortly thereafter Almond³² with zirconates, reacted a bis-triethanolamine metal solution with water and a polyhydroxyl compound to form a new complex which exhibited greater crosslink delay than the component bis-triethanolamine metal crosslinker. The polyhydroxyl compounds (glycerol, mannitol, sorbitol) could be interchanged to regulate crosslink delay times. Aging of the mixture, as mentioned earlier, also played an important role in maximizing the crosslinker's rheological performance.

Putzig and Smeltz,³³ in the mid-1980's, produced an improvement on Conway's and Almond's work by disclosing a method to incorporate alpha-hydroxycarboxylic acids in

addition to the polyhydroxyls and water with a tetravalent titanium compound to produce a more shelf-stable delayed titanate.

Simultaneously with Putzig and Smeltz's disclosures, Ridland and Brown³⁴ were disclosing the very same phenomena with respect to zirconates. Again it was demonstrated that the crosslink times could be controlled by the nature of the polyhydroxyl compound and the alpha-hydroxycarboxylic acid compound employed.

Beta-diketone Complexes of Group 4 Metals. A fourth method of chelation to minimize hydrolysis is to form metal complexes incorporating beta-diketones, such as acetylacetone. Reaction products of titanium alkoxides with acetylacetone have been known at least since the late 1950's.³⁵ Barfuth, et al.³⁶ advanced the effort by disclosing a method for the stabilization of diisopropoxy bis(2,4-pentanedionato) titanium with water by incorporating water into the manufacturing process. Rummo³⁷ disclosed that the simple addition of 2,4 pentadione in conjunction with a Group 4 metal crosslinker could serve to delay the crosslinking reaction rate. Since the Group 4 metal contained in the crosslinker is, in most cases, already fully complexed, the mechanism by which additional "delay agent" causes delay is not well described.

Delaying Gelation with Group 4 Metal Crosslinkers.

Shortly after the introduction of Group 4 metal complexes as crosslinkers for hydraulic fracturing fluids, it was discovered that the nature and extent of gelation prior to the fluid entering the wellbore could dramatically affect ultimate performance of the fluid under downhole conditions.³⁸ Efforts incorporating flow-loops and shear-history simulators began in earnest to determine the extent of these effects. It was discovered that Group 4 metal crosslinkers were more generally more susceptible to shear degradation than either borate or aluminum crosslinked fluids. Since, at that time, Group 4 metal crosslinkers provided greater thermal stability and CO₂ compatibility than either aluminum or borate crosslinked fluids, workers began to search for ways to delay the onset of gelation so as to minimize the shear effects on Group 4 metal crosslinked fluids.

Solutions to cause the crosslinking reaction to be delayed generally took one of three forms: the modification of the crosslinker in manufacturing, the modification of the crosslinker at the district or field location, or the modification of the polymer solution by the addition of additives intended to control the on-set of crosslinking.

Case 1. Crosslinker Modification in Manufacturing. The paper thus far has dealt primarily with modifications that can be made to the crosslinker during manufacture, and how these modifications relate to performance. Modifications at the manufacturing facility are often made to address particular performance attributes, such as delayed or accelerated crosslinker reaction rate, health and safety issues, shelf-life stability, and cost. Incorporating these modifications at the

manufacturing level is the most efficient way to ensure that the product will be consistent. Its biggest drawback is that it is only efficient when the modifications can be incorporated into the manufacture of a large volume of product.

Nevertheless, the ability to incorporate modifications into the manufacture of crosslinkers at the plant level has produced some interesting products. In this fashion, Putz³⁹ developed ethylenediamine and glycine zirconium complexes to produce very slowly hydrolyzing crosslinkers. Conway⁴⁰ developed a polyhydroxyl titanium complex and Almond⁴¹ a polyhydroxyl zirconium complex as a means of producing delayed reaction crosslinkers. Dawson and Le⁴² developed a process for manufacturing a glyoxalated zirconium complex to produce a zirconium crosslinker substantially free of chloride or sulfate ions.

Case 2. Crosslinker Modification in Field Application. Crosslinker modifications at the field level are not uncommon. Variations in field conditions often require that crosslinkers be modified to control the gelation rate of the fracturing fluid. Some of these modifications have involved the reformulation of the crosslinker composition itself.

Hanlon and Almond⁴³ proposed adding additional carboxylic acids, namely citric or malic acid, to a triethanolamine zirconium lactate crosslinker composition as a method to delay the crosslinking reaction rate.

Baranet⁴⁴ disclosed the addition of alkanolamines to zirconium crosslinkers where the ratio of amine to zirconium was at least 15:1 as a means to stabilize the Group 4 metal crosslinker already in aqueous solution, as well as to aid in the stabilization of the crosslinked fluid against shear degradation at high formation temperatures.

Hodge⁴⁵ incorporated the addition of an alpha-hydroxycarboxylic acid, namely hydroxyacetic acid, to commercially available triethanolamine titanate, ammonium titanium lactate, and titanium acetylacetone crosslinkers to produce a more delayed crosslinker.

Case 3. Fluid Additive Effects on Gelation. Another method by which the crosslinking rate can be adjusted is by making modifications to the polymer solution, either by taking advantage of the make-up, water composition and complementing it as Brannon⁴⁶ did, or by adding agents particularly designed to accelerate or delay the onset of gelation, as was proposed by Payne.

Payne⁴⁷ proposed using polyamines, particularly ethylenediamine as a gelation accelerator and aldehydes, particularly glyoxal as a gelation retarder. The author noted, that even where additives were employed to affect the crosslinking reaction rate, that temperature played a role in fixing the crosslink time, e.g., increases in temperature accelerate the crosslinking reaction rate and decreases in temperature retard the reaction rate. The study is particularly noteworthy in that it accentuates the differences in the response of Group 4 metal crosslinkers to various types of amines. In much previous work, it is clear that alkanolamines serve to chelate Group 4 metals, and that the presence of

additional alkanolamine serves to delay the onset of crosslinking, whereas alkylamines, such as trimethylenediamine and triethylentetramine, accelerate the crosslinking reaction rate.

Brannon⁴⁸ disclosed that sodium bicarbonate was particularly useful as a crosslink delay additive for zirconium and hafnium, noting that the mechanism responsible for affecting a delay using the bicarbonate was not understood. Although Brannon offered no hafnium examples, it is fairly well accepted that bicarbonate ions do not play as important a role in causing a delay in the crosslinking reaction rate of titanium crosslinked fluids as with zirconium crosslinked fluids. Brannon noted that it was not simply a matter of pH, in that sodium carbonate additions employed to bring the fluid to the same pH as the bicarbonate addition were not effective. The carbonate-bicarbonate mechanism as it affects crosslinking is under review.

Polymer Considerations

Guar, the principle component of many fracturing fluids, is a high molecular weight polysaccharide derived from the seed of the plant, *Cyamopsis tetragonolobus*. This annual plant grows mainly in arid and semi-arid regions of NW India and E. Pakistan and to a much lesser extent in Texas. Guar is grown principally as a food crop for animals and an ingredient in human foods. The guar plant is pod-bearing, with each pod containing six to nine seeds per pod. Each seed is composed of hull (approx. 15%), germ (approx. 45%) and endosperm, (approx. 40%). The endosperm is comprised predominately of the guar galactomannan.

Guar is comprised of a linear chain of D-mannose residues with D-galactose units, connected, on average, to every second chain mannose unit. However, as uniform as a description of the polymer might make it appear that all guar should perform equally well, commercially available high viscosity materials suitable for use in fracturing may differ considerably in their moisture content, insoluble-residue, ash weight, hydration rate, bacterial count, etc. These differences contribute to variation in the rheological performance of the polymer solution, and ultimately to its rheological performance upon gelation. While guar hydrates well in aqueous solutions, concerns about clarity and improved thermal stability led to the development of a number of chemically modified guars.

It was illustrated in SPE 39531 that even though a derivatized guar may be described as having some particular chemical composition, the reality is that its performance in a fracturing fluid composition may vary widely. Not only are the very same factors that affect guar performance present to affect the rheological performance of its derivative, there are derivatization reaction by-products that can detrimentally affect the performance of the crosslinked fluid. For instance, sodium tetraborate is typically used as a processing aid in the manufacture of derivatized guars. In certain instances, such as with deep well treatments where the polymer loading may be considerable (say above about 50 lbs. per 1000 gals.) and the fluid pH considerably alkaline (> 9.5) to enhance the gelled fluid rheology once it has entered the formation, premature

gelation may occur. While it has not been established that premature gelation brought on by borate complexing may result in shear degradation of the crosslinked fluid, it is well accepted that premature gelation may result in excessive surface treating pressures and therefore greater treatment costs.

Similarly, derivatization reaction by-products, such as the formation of hydroxycarboxylic acid salts (e.g., sodium glycolate) can affect crosslinker demand by providing additional chelation opportunities for the crosslinking metal. Removal of these by-products may produce a guar derivative that requires lower crosslinker or polymer loadings to achieve the same gelled fluid performance.³⁹

Polymer Crosslinking Mechanisms. Several models have been hypothesized to describe the interaction between transition metals (and borates) and polygalactomannans.³⁰ Recently, however, Chandrasekaren et al.³¹ reported "the first visualization of ion-mediated crosslinking of substituted (CMHPC) chains." Using molecular modeling software, Chandrasekaren was able to energetically define favorable crosslinking sites for CMHPC and a divalent ion. The "nest" of up to six bonding sites can exist between two CMHPC chains and involves carboxylate oxygen atoms.

Conclusions

The information contained in this paper is the accumulation of many years of analytical evaluation and experience with Group 4 metal complexes as crosslinkers for polygalactomannans. Our conclusions, are therefore, the direct result and the best effort of our first attempt at consolidating these laboratory evaluations and field experiences into a "system," with which we hope to be able to demonstrate that crosslinker structure can be correlated with rate of gelation performance. Although we hope to be able to use the work we report here as a basis for a more thorough examination of certain aspects of polymer crosslinking for oilfield applications, we readily admit that the work presented here is not the result of a well-defined experiment with the intention of producing an inarguable conclusion. Having said that,

1. Water-soluble compounds of Group 4 metals generally hydrolyze upon addition to water to form oligomers.
2. The rate at which water-soluble Group 4 metal compounds oligomerize is related to the extent and method by which they are complexed.
3. Aqueous-stable Group 4 metal complexes are formed by complexing (chelating) the metal by various methods with an alkanolamine, an alpha-hydroxycarboxylic acid, a polyhydroxyl compound, a beta-diketone, or a combination of these agents.
4. Relative rate of gelation performance can be correlated with Group 4 metal crosslinker structure.

5. Modifications to crosslinker structure to affect rate of gelation performance can be made in manufacturing, to the crosslinker in the field, or to the fracturing polymer solution.
6. Attributes of the polymer may play a considerable role in the rate of crosslinking, the amount of crosslinker required to achieve gelation, and to the rheological performance of the crosslinked fracturing fluid.

As a result of the effort here, the authors believe that there are several areas that are particularly suited for further examination with respect to Group 4 metal crosslinkers. These include:

1. An explanation as to why alkanolamine zirconium complexes crosslink at a slower rate than the corresponding titanium complex;
2. A correlation between the nature of an alkanolamine, carboxylic acid, polyhydroxyl compound, carbonate/bicarbonate salt, and/or diketone and the gelation rate;
3. The mechanism by which additional "delay agent" beyond that already incorporated into the structure of the crosslinker serves to affect the gelation rate;
4. A greater understanding into the crosslinking mechanism of Group 4 metal crosslinkers with polygalactomannans.

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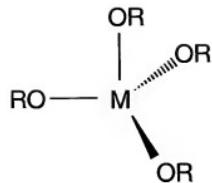
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Table 1. Crosslink Time Test Results

			pH 5	pH 7	pH 9	pH 11
1.	2 nd AmineOH Zr Lac, 5.03% Zr (0.25 ml/250 gms)	T1 T2 Temp Quality	32 300+ 40C weak	11 16 27C good	5 7 25C strong	2 5 25C v. strong
2.	3 rd AmineOH Zr Lac, 4.52% Zr (0.244 ml/250 gms)	T1 T2 Temp Quality	300+ 300+ 45C v. weak	240 300+ 45C weak	150 300+ 45C good	16 70 28C strong
3.	Mixed Amine Zr Lac, 5.16% Zr (0.278 ml/250 gms)	T1 T2 Temp Quality	7 11 28C good	6 9 27C v. good	4 7 26C strong	3 6 25C v. strong
4.	3 rd AmineOH Zr 4.29% Zr (0.293 ml/250 gms)	T1 T2 Temp Quality	35 90 25C good	25 70 25C strong	21 55 25C strong	11 21 25C v. strong
5.	Na Zr Glycolate 5.2% Zr (0.242 ml/250 gms)	T1 T2 Temp Quality	300+ 300+ 40C no gel	21 300+ 40C v. weak	7 11 25C v. strong	2 5 25C broken
6.	Na Zr Lac I 5.18% Zr (0.243 ml/ 250 gms)	T1 T2 Temp Quality	1 2 40C weak	1 2 25C weak	1 4 25C v. strong	1 3 25C v. strong
7.	Na Zr Lac II 5.4% Zr (0.233 ml/250 gms)	T1 T2 Temp Quality	25 230 40C good	10 15 27C v. good	1 4 26C v. strong	<1 2-3 25C v. strong
8.	NH4 Zr Citr 5.18% Zr (0.243 ml/ 250 gms)	T1 T2 Temp Quality	300+ 300+ 25C no gel	300+ 300+ 25C no gel	300+ 300+ 25C no gel	300+ 300+ 25C no gel
9.	AmineOH Zr 12.4% Zr (0.101 ml/ 250 gms)	T1 T2 Temp Quality	300+ 300+ 45C no gel	300+ 300+ 45C v. weak	290 300+ 40C weak	34 100 30C good

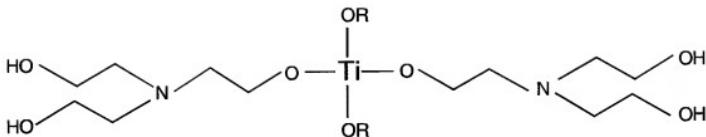
			pH 5	pH 7	pH 9	pH 11
10.	AmineOH Zr 13.2% Zr (0.095 ml/ 250 gms)	T1 T2 Temp Quality	25 51 25C good	16 25 25C v. good	11 21 25C strong	7 10 25C v. strong
11.	Ti Lac/sorbitol 3.54% Ti (0.187 ml/ 250 gms)	T1 T2 Temp Quality	21 300+ 45C weak	17 300+ 40C good	5 11 25C strong	1 6 25C broken
12.	2TEA Ti from 4n-butyl alkoxide 7.5% Ti (0.088 ml/ 250 gms)	T1 T2 Temp Quality	3 5 25C strong	1 3 25C strong	1 3 25C v. strong	1 3 25C broken
13.	2TEA Ti from 4-isopropyl alkoxide 7.5% Ti (0.118 ml/ 250 gms)	T1 T2 Temp Quality	3 7 25C strong	2 5 25C strong	1 3 25C v. strong	1 3 25C broken
14.	2TEA Ti (aqueous) 8.3% Ti (0.08 ml/ 250 gms)	T1 T2 Temp Quality	3 5 25C good	2 4 25C strong	1 3 25C broken	1 1 25C broken
15.	Na Hf Lac 5.9% Hf (0.414 ml/ 250 gms)	T1 T2 Temp Quality	300+ 300+ 40C good	25 57 25C good	4 7 25C v. strong	2 4 25C v. strong

Crosslink time tests were vortex closure tests conducted by the method described by Hodge in SPE 16249, "Evaluation of Field Methods to Determine Crosslink Times of Fracturing Fluids." T1 corresponds to the vortex closure time, T2 to the time required to produce a "lip." Times are reported in seconds. Crosslink times greater than 5 minutes are reported as 300+. All tests were conducted at ambient laboratory conditions. Reported Temp is the temperature required to produce a "lip." The Quality of the gel is, of course, a subjective interpretation. The pH was adjusted with either hydrochloric acid or sodium hydroxide solution. No effort was made to buffer the solution or modify the crosslinker to cause changes in the crosslinking reaction rate. Every effort was made to insure that the same number of Group 4 metal molecules were added as crosslinker in each test, regardless of the nature of the Group 4 metal. The ratio shown in brackets, e.g. 0.25 ml/250 gms, represents our best effort at assuring that all crosslinkers were evaluated on the same basis. This was the crosslinker loading used to conduct the crosslink time tests for that particular crosslinker.



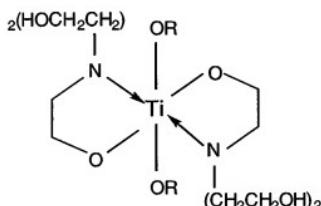
M = Ti (titanium), Zr (zirconium), Hf (hafnium)
R = alkyl, aryl

Figure 1. Group 4 metal alkoxide



R= isopropyl, butyl or 2-ethylhexyl

Chrisp's original interpretation of titanium triethanolamine chelate



Chrisp's original interpretation of titanium triethanolamine chelate re-drawn to reflect a cage-like structure

Figure 2. Chrisp's bis-triethanolamine titanate

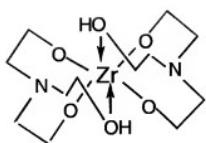


Figure 3. bis-triethanolamine titanate characterization by proton and C-13 NMR

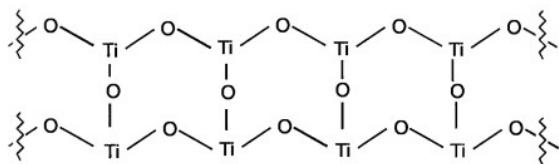


Figure 4. Oligomeric Titanium oxide chain

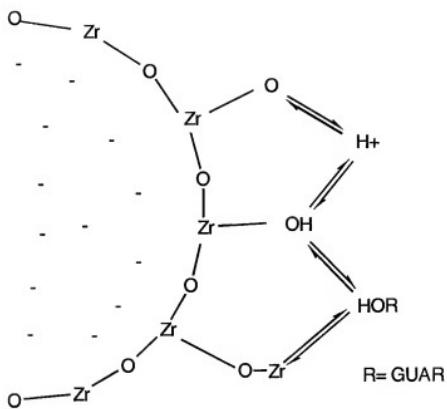


Figure 5. Zirconium colloidal structure and possible bonding mechanism with guar
(after Kramer & Prud'homme, SPE 16914)

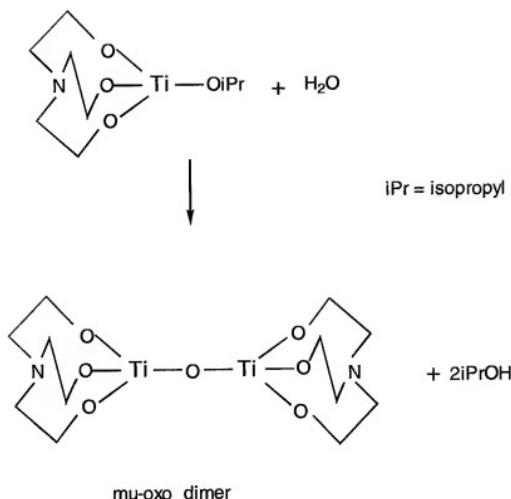


Figure 6. The addition of water to mono-triethanolamine titanate to form a mu-oxo dimer

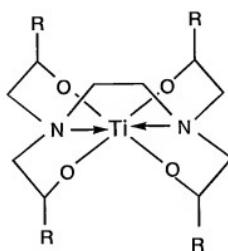


Figure 7. Tetra-hydroxyalkylated ethylenediamine complex of titanium

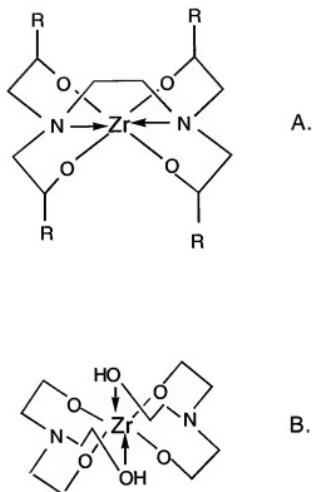


Figure 8. Structural comparison between tetra-hydroxyalkylated zirconate complex (A) and the bis-triethanolamine zirconate complex (B)

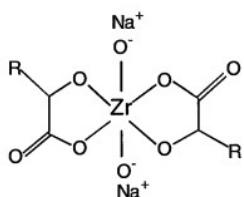


Figure 9. Sodium zirconium dicarboxylate

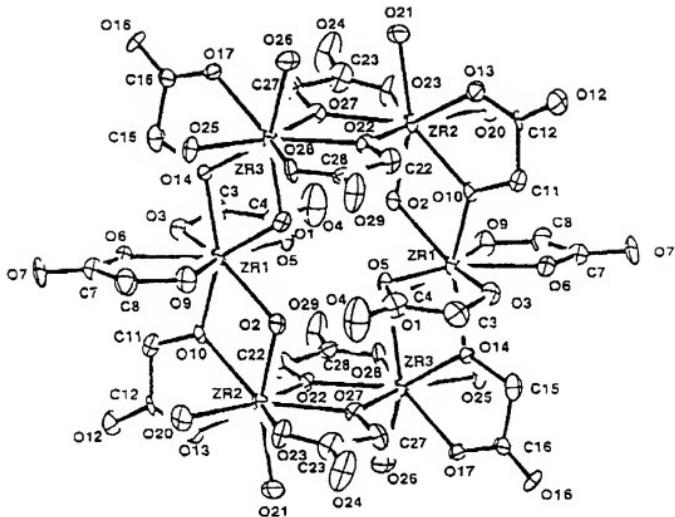


Figure 10. Thermal ellipsoid plot for $\overbrace{[(\text{CH}_2(\text{OH})\text{C}(\text{O})\text{O})_2\text{Zr}(\text{OH})_2]} \cdot 14\text{ H}_2\text{O}$
(waters of crystallization omitted)